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14. ABSTRACT

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Chemical patterning of silicon dioxide substrates for selective deposition of gold nanoparticles and fabrication of single-electron transistors

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ABSTRACT: We describe a novel method to pattern SiO_2 surfaces with colloidal gold nanoparticles by e-beam lithography and selective nanoparticle deposition. The simple technique allows us to deposit nanoparticles in continuous straight lines, just one nanoparticle wide and many nanoparticles long. We contact the pre-positioned nanoparticles with metal leads to form Single Electron Transistors (SETs). The Coulomb blockade pattern surprisingly does not show the parasitic "random charges" at low temperatures, indicating relatively little surface contamination.

Single Electron Transistors (SETs) are three-terminal devices, made of a central island (e.g. nanoparticle) contacted by two tunneling electrodes (*source* and *drain*) and electrostatically coupled to the *gate* electrode. At low temperatures, the source-drain current through the island is typically blocked, since the energy required to add just one extra electron to the nanoparticle may be large. However, one can tune the electrostatic potential of the nanoparticle by biasing the nearby gate, so that an extra electron may be added/removed to/from the central island without an energy cost, and electrons may flow through the structure. The phenomenon of Coulomb blockade, described above, may have interesting technological applications if the charging energy of the SET is increased by reducing the size of the central island.

A number of experiments have studied SETs with the central island made of individual nanoparticles and even molecules. OR: Single Electron Transistors made of individual nanoparticles [1-10] or even molecules [11] have been fabricated before. In making the SET, the main challenge is to position the nanoparticle in the nanoscale gap between the source and the drain electrodes. Typically, the nanoparticles are either deposited randomly [1, 3, 4, 7, 10], or attracted to the gap by a large electric field gradient [2, 5, 6, 8, 9]. Most recently, contacts were made to a chain of nanoparticles pre-formed in solution and randomly deposited on SiO_2 surface [12]. Here, we describe a novel method to reliably fabricate SET by positioning the nanoparticles at the desired positions on the SiO_2 surface.

We have developed a technique to attract gold nanoparticles at the chemically functionalized locations on the SiO_2 surface. We define the desired pattern on the surface by e-beam lithography and treat it with APTES (aminopropyltriethoxysilane). APTES covalently attaches to the surface and displays positively charged amine groups. These groups in turn attract the negatively charged citrate-stabilized colloidal gold nanoparticles [13]. In Figure 1a we demonstrate high deposition specificity and good surface coverage achieved by of our method. In Figure 1b, the surface was successively patterned with horizontal lines of 13 nm particles and then with vertical lines of 50 nm particles. Clearly, the particle attachment to the surface is rather strong: the 13 nm particles stayed on the surface throughout the second patterning stage and deposition of 50 nm particles.

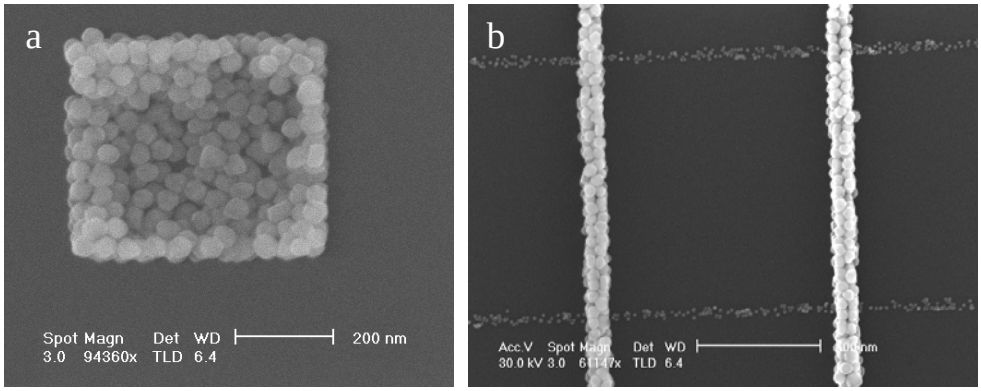

Figure 1. a) 50 nm gold nanoparticles are selectively deposited in a rectangular shape. Scale bar: 200 nm. b) Lines of 13 and 50 nm nanoparticles are successively patterned. Scale bar: 200 nm.

We start by describing our protocol for the surface patterning with APTES and nanoparticle deposition. The process consists of 3 main steps: 1) e-beam lithography to define the desired patterns in PMMA on the Si/SiO_2 substrate, 2) surface treatment with APTES and 3) deposition of Au nanoparticles. The details of each stage are outlined below:

1) The samples were fabricated on highly p-doped silicon substrates capped with a 1000 nm oxide. The wafers are cleaned using the standard SC1/SC2 (RCA) processes to remove organic and inorganic contaminants from the surface [14]. The substrates are then spin-coated with PMMA (typically 495k or 950k molecular weight) and a pattern is drawn on the sample surface by the electron beam (30 keV). The width of the lines is partially determined by the line dosage of the e-beam. The exposed PMMA is developed with MIBK:IPA 1:3 leaving behind the desired patterns (e.g. trenches).

2) 10μL of APTES in 1% aqueous solution is deposited on the 5x5 mm^2 substrate for 10 minutes. Thereafter, the APTES is rinsed off in DI water, leaving behind a thin layer of APTAS covering the exposed SiO_2 surface. In our experience, longer incubation times or higher APTES concentrations resulted in formation of a thicker APTES layer and poor nanoparticle adhesion to the pattern.

3) 10 μL of colloidal NP suspension (13 nm or 50 nm in diameter) is then deposited on the substrate. It is important to sonicate the suspension before it is applied to the substrate. Sonication breaks up the nanoparticles clusters, which would otherwise be deposited in large clumps/ dendritic chains. After 10 minutes, the suspension is rinsed off in DI water. The sample is then immersed in hot acetone for PMMA liftoff and finally rinsed in methanol. At this point we inspect the sample with the Scanning Electron Microscope to observe the gold nanoparticles forming the desired patterns on the sample surface.

Our method is similar to the technique used in Ref. [15] to deposit DNA rafts on the self-assembled APTES monolayers patterned by e-beam lithography. In both cases, the positively charger amine groups of APTES attract the negatively charges objects (nanoparticles or DNA). The two methods differ in the sequence of two major steps: while we apply the nanoparticles to the SiO_2 surface still covered with APTES, the authors of Ref. [15] apply the DNA once the surface was stripped of PMMA.

We have conducted systematic comparison of various deposition schemes to determine the optimal sequence of fabrication steps. Most thoroughly, we concentrated on the following recipes: **a**) the “standard” method as described above; **b**) control deposition with no APTES; **c**) APTES is applied before PMMA and e-beam lithography (steps 1 and 2 above are interchanged); **d**) after the APTES treatment, PMMA is striped off, followed by the nanoparticle deposition. The last protocol is similar to the one described in Ref. [15]. For each recipe, we performed the same steps with nanoparticles of different sizes and with different lithographic patterns. Our conclusions are as follows: recipe **b**) results in much low concentration of particles than recipe **a**); recipe **d**) results in some particles randomly attached outside of the desired pattern; recipes **a**) and **c**) work equally well. Depending on the applications, it may be desired not to expose the entire SiO_2 surface to APTES. We therefore stick to “standard” recipe **a**) for the rest of the paper.

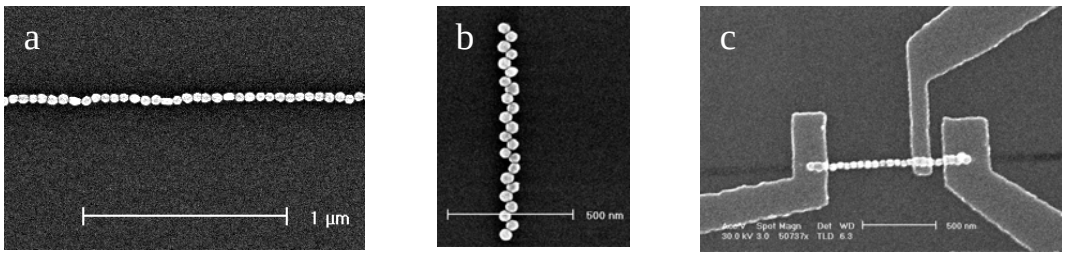

Figure 2. a) Gold nanoparticles are selectively deposited on the surface along a patterned line. b) By controlling the width of the line, more complex structures are achieved. c) Contacts to the particles are made by e-beam lithography.

The primary aim of this paper is to fabricate functional Single-Electron Transistors from one or several interconnected nanoparticles. Using the optimized protocol, we routinely produce linear chains just one nanoparticle wide and tens of nanoparticles long (Figure 2a, b). In the final e-beam lithography step we place two or more metal contacts across the nanoparticle chain (Figure 2c). Using e-beam lithography, it is straightforward to make pairs of electrodes separated by gaps of tens of nanometers. Many of these electrode pairs will be bridged by just one nanoparticle, thereby forming Single-Electron Transistors.

At low temperatures, the conductance of nanoparticles contacted by a pair of electrodes demonstrates a clear Coulomb blockade pattern. Many single-electron conductance oscillations are visible as a function of gate voltage (Figure 3a). These data show very good reproducibility of the peak positions when the gate voltage is swept in different directions. Particularly noticeable is the lack of the "offset charges", which create discontinuous shifts of the

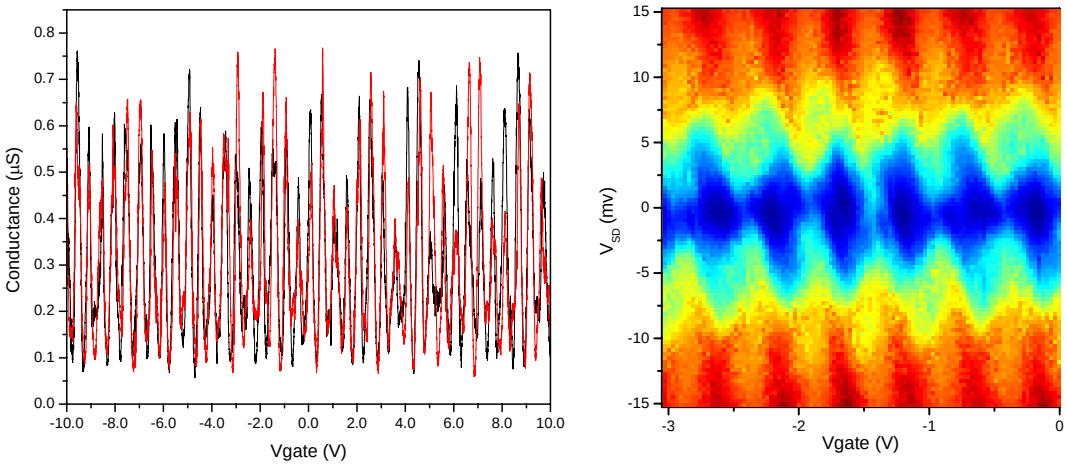

Figure 3. Left: Coulomb blockade pattern in differential conductance G=dI/dV measured as a function of gate voltage, Vgate, at 4.2 K. Note, that positions of the peaks coincide in the two superimposed traces, which were swept successively in opposite directions. This is an indication that the "offset charges", that rigidly shift the segments of the G(Vgate) curve are absent. Also noticeable is the width of the peaks, greatly exceeding the possible temperature broadening. The width is explained by the lifetime broadening, which indicates low tunneling barriers and good coupling of the nanocrystal to at least one of the leads. Right: "Coulomb diamonds" in conductance measured as a function of the gate voltage and the source-drain bias. Note the smooth pattern, again lacking the rigid "offset charging" events. Colormap: 0  2.2 µS.

conductance curves at random values of gate voltage. The offset charges are detrimental to the reliable operation of the Coulomb blockade samples. Their absence indicates that the sample surface is relatively free of contaminants, which can be randomly charged or discharged. APTES treatment makes SiO_2 surface hydrophobic; we surmise that its water repellent effect may help to reduce the offset charges.

Finally, Figure 3b shows the conductance map of the same sample, measured as a function of the gate voltage and the source-drain bias. Here, we rapidly sweep the source-drain bias as the gate voltage is slowly changing. The offset charges would result in discontinuous vertical lines in the conductance map; the observed smooth conductance map clearly indicates the lack thereof.

In conclusion, we have developed a simple and efficient method to pattern SiO_2 surface with colloidal gold nanoparticles. We use this recipe to produce single-particle lines and to fabricate SET at the desired locations on the sample surface. Eventually, we plan to develop this method in conjunction with that of Ref. [15] to deposit nanoparticle assemblies anchored to DNA scaffold.

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